

CELLULOSE CHEMISTRY: PERSPECTIVE AND RETROSPECT

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ABSTRACT

Cellulose and the related polysaccharides found in plant cell walls, historically, have provided raw materials for many of mankind's requirements. Due to the increasing demands caused by the expanding population, rising economy and developing technology, during the 20th century, these renewable materials are no longer considered as inexhaustible. Under these circumstances the public sentiment is turning more and more towards the conservation, efficient utilization and reduction of waste. Wasteful practices such as burning substantial quantities of cellulosic materials without due concern for environmental degradation are no longer acceptable.

The increasing concern for safety and quality of the environment and development of a multi-disciplinary approach towards the chemistry of natural products indicate that in future research programmes more emphasis should be placed on investigation and understanding of the cell-wall polysaccharides as a significant biological material and environmental substrate rather than an abundant raw material or a chemical commodity.

Plant cells are distinguished from animal cells by the presence of true cell walls containing polysaccharides. In higher plants (*Embryophyta*) and a majority of lower plants (*Thallophyta*), cellulose forms the principal structural component of different layers and lamellas of the cell wall which are further interlaced with a variety of matrix polysaccharides and often are impregnated with lignin¹.

Different applications of the naturally available cellulosic materials have produced a profound influence in shaping the destiny of man and the development of its science, technology and economics. We are witnessing a period within the sequence of these interrelated developments, when the established concepts and methods are changing rapidly. Therefore, it will be interesting to glance through various aspects of the chemistry and technology of cellulose to see how they have developed and what is their new direction and emphasis.

COMBUSTION OF CELLULOSIC MATERIALS

The readily available cellulosic materials, historically, have provided an abundance of natural fuel for mankind. As ancient man spread out from his

original habitat in tropical forests to occupy virtually all the earth, he seems to have made campfires for protection and supplementary heat. Use of fire as well as stone tools and language probably distinguished mankind from other primates by the beginning of the Pleistocene era^{2, 3}. The most momentous chemical event in development of mankind must have been the discovery of a method for generating fire through the ignition of vegetation or cellulosic material⁴. If one believes in Greek mythology, Prometheus, who taught mankind the use of fire and was punished by Zeus for stealing it from heaven, must be considered the first chemist. On this basis, cellulose chemistry must be accepted as the forerunner of our science and technology. Useful application of fire by early man led to the development of the arts of baking and pottery and to the refining of gold, silver and other metals⁴. Fire has been also used as an environmental tool to open up thick forests for easier hunting and collecting and to clear the land for agriculture and herding. Partial combustion of wood led to charcoal-making and wood distillation which until recently were used to obtain wood alcohol, tar and other chemicals. Cellulosic materials are also adapted as fibre for clothing and as wood for shelter. During the recent World Wars they were even used as a source of sugar and food.

In the 20th century, the use of wood or cellulosic materials as fuel has gradually diminished. However, their application for production of paper, one of the basic materials of modern civilization, has increased overwhelmingly (*Table 1*)⁵.

Table 1. World production of paper and paperboard

Year	America	Europe	Others	Total
1913	6	6	1	13
1935-1938 (average)	16	12	3	31
1946	24	8	2	34
1947	26	9	2	37
1948	27	10	3	40
1949	26	11	4	41
1950	30	13	4	47
1951	32	14	5	51
1952	30	13	6	49
1953	32	15	6	53
1954	33	17	6	56
1955	36	18	9	63
1956	38	19	9	66
1957	37	20	11	68
1958	37	21	11	69
1959	40	22	14	76
1960	41	25	15	81
1961	43	26	17	86
1962	45	27	17	89
1963	48	29	19	96
1964	51	31	21	103
1965	54	32	23	109
1966	56	34	26	116
1967	56	35	26	117
1968	59	37	28	124

CELLULOSE CHEMISTRY

The increasing demand for wood, caused by the expanding population, developing technology and rising economy, has been so great in recent years that these renewable raw materials are no longer considered as inexhaustible. Under these circumstances social sentiment is turning more and more towards conservation and efficient management of the remaining forests and forest products.

The statistics for timber cut in the United States are shown in *Table 2*⁶. The data show that more than 1.23 billion cubic feet of timber is wasted as the logging residue before reaching the processing plants. Of the 5.6 billion cubic feet of veneer and saw logs which are processed in the plants, about 2 billion cubic feet end as waste or hog fuel (*Table 3*).

Table 2. General statistics for timber cut from growing stock in USA.

Product	Statistics			Projections		2000
	1952	1962	1970	1980	1990	
Sawlogs:						
Softwoods	4602*	3947	4120	4460	4910	5490
Hardwoods	1199	989	1030	1120	1230	1380
Total	5801	4936	5150	5580	6140	6870
Veneer logs:						
Softwoods	219	579	930	1120	1350	1630
Hardwoods	173	146	180	230	290	350
Total	392	725	1110	1350	1640	1980
Pulpwood:						
Softwoods	1407	1725	1980	2720	3410	4420
Hardwoods	248	628	960	1480	2110	2970
Total	1655	2353	2940	4200	5520	7390
Miscellaneous industrial wood:						
Softwoods	278	203	200	200	200	200
Hardwoods	301	177	170	170	170	170
Total	579	380	370	370	370	370
Fuelwood:						
Softwoods	232	93	80	60	50	40
Hardwoods	734	424	370	310	260	210
Total	966	517	450	370	310	250
Total timber products:						
Softwoods	6738	6547	7310	8560	9920	11780
Hardwoods	2655	2364	2710	3310	4060	5080
Total	9393	8911	10020	11870	13980	16860
Logging residues:						
Softwoods	749	644	640	730	790	890
Hardwoods	615	593	650	760	890	1070
Total	1364	1237	1290	1490	1680	1960
Total timber cut:						
Softwoods	7487	7191	7950	9290	10710	12670
Hardwoods	3270	2957	3360	4070	4950	6150
Total	10757	10148	11310	13360	15660	18820

* Growing stock—million cubic feet.

F. SHAFIZADEH

Table 3. Wood residues produced in the US processing plants in 1962 (million cubic feet)

	Softwood	Hardwood	Total
Plant residues	2136	607	2743
Used for pulp	651	57	708
Used for fuel, etc.	542	221	763
Unused	943	329	1272

Used paper products also constitute a major source of cellulosic waste. The total residential, commercial and industrial solid waste produced in the United States amounts to 1.38 billion pounds per day. The municipal residues, which amount to 1.02 billion pounds per day, contain on the average 55% paper, much of which is burned or buried⁷.

Better utilization of the cellulosic materials is taking a new dimension not only because of the shortage of raw materials and inroads into the natural resources, but also because of the detrimental environmental effects produced by burning as the traditional waste disposal method. With the recent upheavals, open burning of the slash in forest lands and industrial and household residue in urban areas are no longer socially acceptable and the alternative methods of disposal are often economically impractical.

Conservation of natural resources and concern for safety of the natural and urban environments also relate to the problems of fire and combustion of cellulosic materials in a more direct manner. An estimate of fire losses for 1968-69 in some parts of the world is given in Table 4^{2, 8}. In the United States alone the losses amounted to more than 12000 lives, scores of non-fatal

Table 4. Fire statistics for 17 countries.

Country	Year	Pop. in thousands	No. of fire deaths	No. of fires	Loss in US dollars (thousands)
Australia	1969	12099	196	86000	102273
Austria	1969	7349	88	9329	22379
Belgium	1969	9630	76	11641	no data
Canada	1969	21007	624	64667	180511
Denmark		4870	77	12949	43924
Finland	1969	4688	110	11900	12600
France	1968	49795	219	62206	190036
Italy	1969	53648	no data	48180	no data
Japan	1969	101090	1334	56304	189221
Netherlands	1969	12798	73	17779	49815
New Zealand	1969	2776	33	15657	9036
Norway	1969	3819	85	10000	45080
Sweden	1969	7950	110	20000	48275
Switzerland	1968	6071	no data	7418	12344
United Kingdom	1969	55272	987	253225	288960
United States	1969	203000	12200	2425350	2447600
West Germany	1969	59872	no data	366000	289170

injury and nearly 2.5 billion dollars worth of property, without counting the cost of protection and insurance. In the same year, wild fires burned 6.9 million acres of forest and wildland. Most of these fires involved cellulosic materials and natural fuels.

Attempts to control hazardous fires by flame proofing of cellulosic materials dates back to the early civilizations. It is reported that Egyptians treated wood with alum. The process was refined by Gay-Lussac who treated samples of linen and hemp cloth with different salts and found the presently used chemicals, ammonium phosphate and borax, to be more effective^{2, 9, 10}. To bring the technology up to date, cellulose chemists should define the chemical transformations involved in initiation, propagation and termination of flaming cellulose combustion as a basis for future scientific rather than empirical progress on this subject.

If past history is an indication for the future, in the long run the problems of safety and quality of the environment which are facing our generation, can not be solved by political pressure, restrictive legislation, special privileges or shoddy practices. The ultimate solution lies in understanding the basic principles involved and their intelligent application to our social needs. This theory could be verified by two thousand years turbulent history of paper making which like the combustion of cellulosic materials is interwoven with the course of our civilization.

PULP AND PAPER INDUSTRY

Before the discovery of paper, people were using papyrus, parchment (vellum), cloth, bark and even clay tablets and stone for recording their thoughts. The original discovery of paper is attributed to Ts'ai Lun in the year 105 A.D.¹¹⁻¹³. Ts'ai Lun was seeking a substitute for the costly silk and strips of bamboo or wood which were used for writing and drawing in China at the time. He meditated and laboured, as a true researcher, to produce paper from pulped bark fibre, old rags and discarded fish nets. The paper industry was established in China using hemp, bark or paper mulberry (*Broussonetia papyrifera*) and bamboo as raw materials. Pieces of bamboo were soaked for more than one hundred days and boiled in milk of lime for approximately eight days and nights. By the caravan route through the Gobi Desert and Samarkand, the Chinese supplied paper to Persia but tried to keep the process secret. During a battle fought in 751 on the banks of the Tharaz River in Turkestan, several skilled paper workers were taken prisoner and put to work in Samarkand. From there the knowledge of paper-making spread through Persia to Bagdad and Damascus, acquiring considerable refinements and reaching Morocco by about 1100.

The Moors took the industry to Europe in the 12th century and established paper-making centres in Játiva, Valencia and Toledo. Also, through the Arab occupation of Sicily, paper-making spread to Italy, Switzerland and southern France, despite an initial resistance to accepting the devices of the Infidels. Emperor Frederick II, who was in trouble with Pope Gregory IX for dragging his feet during the Crusades, in 1231 forbade the use of paper for public documents. The watermark which first appeared in the form of a

cross in paper made in Italy in 1282 and subsequently took other forms of Christian symbolism gave the Infidels' product a blessed acceptance. Acceptance of paper and spread of the paper industry in Europe created a chronic shortage of rag that was used as the raw material. The Venetian senate in 1366 granted paper-makers of Treviso a monopoly of rag collection to protect them from the exaction of rag pickers. In Basel, authorities gave the local industry the first right for buying rags. The rag famine and shortage of paper became so acute, especially after the development of printing in the 15th century, that various establishments resorted to strong measures. To relieve the situation, the chapter of St. Hilaire of Angoulême converted its flour mill into a paper mill. The University of Paris obtained tax exemption and special privileges for its suppliers from John the Good, and Charles VIII in 1489 confirmed these privileges. In 1666 the English parliament passed a law that only wool could be used in burial shrouds. This law was supposed to help the wool industry with a new market and save linen and cotton for the paper makers.

There are many interesting stories about the shortage of paper during the American Revolution and Civil War including the use of the woven wrappings and the papyrus fillings of imported Egyptian mummies by a Maine paper manufacturer named I. Augustus Stanwood to produce a coarse brown wrapping paper. This enterprise is said to have caused the spread of a cholera epidemic amongst the mill workers.

The shortage of paper eventually was relieved by production of pulp from wood which was responsible for literally raising the industry from rags to riches. The rapid expansion of the industry in the 20th century, as shown in *Table 1*, has now created the reverse problem of waste. The credit for starting this immense industry is obviously shared by many scientists and inventors, but it is interesting to note that the seeds for the idea of extracting the cellulosic fibre from abundant woody tissues not only could be found in the Chinese practice of boiling bamboo in milk of lime but also in a treatise submitted to the French Royal Academy by René Antoine Ferchault de Réaumur on November 15, 1719. In this treatise, Réaumur, a noted physicist and naturalist observed that 'The American wasps form very fine paper, like ours; they extract the fibres of common wood of the countries where they live. They teach us that paper can be made from the fibres of plants without the use of rags and linen, and seem to invite us to try whether we cannot make fine and good paper from the use of certain woods.'

Another 120 years elapsed before the French chemist Anselme Payen demonstrated that a fibrous substance which he called cellulose (in 1839) could be isolated by treatment of wood with nitric acid. Isolation of this substance opened the door for production of wood pulp by commercial methods of delignification including soda processes patented by Watt and Burgers (1853), the sulphite process invented by Tilgman (1866), the Kraft process developed by Eaton (1870) and Dahl (1884) and various bleaching methods. Numerous refinements and developments of these processes in the 20th century has lead to the rapid growth of this industry and adaptation of paper not only for writing and printing but also for wrapping, packaging and a variety of disposable products. At this juncture the research emphasis does not seem to be focused on further refinements but in solution of the environmental problems caused by malodorous sulphur compounds, thermal

and other forms of water pollution and increasing amounts of solid waste. Under these circumstances various problems of recycling and alternative methods of delignification such as oxygen pulping are being seriously investigated.

STRUCTURE, MORPHOLOGY AND BIOGENESIS OF CELLULOSE

Isolation of cellulose from plant tissues by the laboratory and industrial processes naturally focused the scientific interest on defining the structure, composition, properties and the biogenesis of this material. It is interesting to note that after more than a century of scientific investigation and numerous findings, controversies and debates, the term cellulose (in pure form) still means different things to different groups. To the organic chemists it means β -D-(1 \rightarrow 4)-linked glucopyran. To the technologists it means an asymptotic entity, often called α -cellulose, which represents the alkali insoluble portion of the wood pulp. To the biologists it means the fine microfibrils of plant cell walls which reach a high degree of purity and perfection in a group of green algae, including *Valonia*, *Cladophora* and *Chaetomorpha*, as shown in Figure 1^{1, 14}. These groups have been concerned not only with the chemical structure of cellulose and its reactions, but also with its interrelated physical, morphological and biological properties. Through various types of inquiries they have tried to find how cellulose is crystallized and packed in the fibrils to give it the fibrous and physical properties; what are the fibrils and microfibrils and how they are organized within the layers and lamella of the cell wall; whether the microfibrils are produced and organized by inanimate physical forces or by the direct biological influence of the living cell.

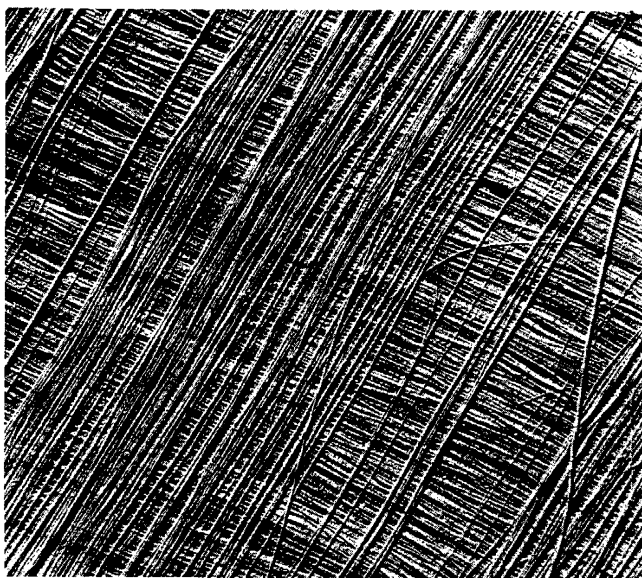


Figure 1. Cellulosic orientation of microfibrils in the cell wall of *Chaetomorpha melanogonium* shown in a micrograph by Frei and Preston¹⁴.

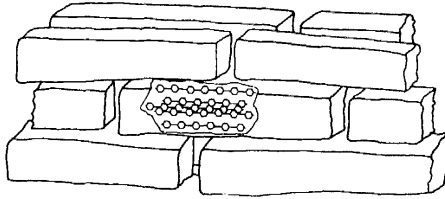


Figure 2. The original concept of the brick-like structure of cellulose fibres¹⁵.

About 20 years after the isolation of cellulose by Anselme Payen, Carl Nägeli¹⁵ attributed the birefringence of the cell walls observed under the polarized microscope to the presence of separate brick-like crystalline micelles within the cellulose fibres, as shown in *Figure 2*. The next step in this direction awaited the application of x-ray techniques which confirmed the

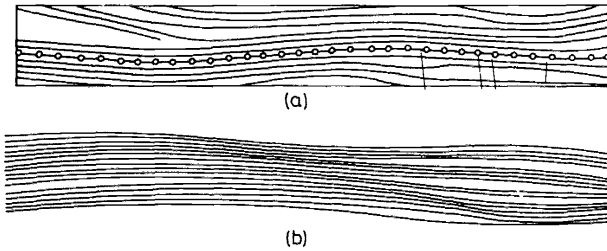


Figure 3. Arrangement of cellulose molecules according to the fringed micellar theory (a) and the continuous concept (b).

crystallinity of native cellulose. Interpretation of the x-ray data culminated in the assignment of cellulose I crystalline structure for native fibre and cellulose II for the regenerated material. In cellulose II it was assumed that the molecular chains are antiparallel because arrangement by crystallization would be statistically less likely. This conclusion was also extended to cellulose I because the data would fit. Furthermore, it was assumed that the diffusion and broadening of the x-ray diffraction lines represent micelles of about 5 to 10 nm in diameter and 50 to 60 nm in length, embedded in amorphous materials, according to the prevailing micellar concept. Organic chemists confirmed this concept by application of end group analysis, indicating a degree of polymerization (D.P.) of 100 to 200 for cellulose which was in close agreement with the value of 120 estimated from the x-ray data. Later, when viscosity measurements and ultracentrifuge studies showed increasing D.P. values of 3000 and 10000 for native cellulose, the original micellar theory became no longer tenable and was modified to fringed micellar theory¹ rather than being abandoned. In this modification (see *Figure 3*) it is assumed that a single cellulose chain passes through several crystalline and amorphous areas. This theory, which explained many physical and chemical properties of cellulose including the moisture absorption and partial acid hydrolysis to individual micelles, became the rallying

CELLULOSE CHEMISTRY

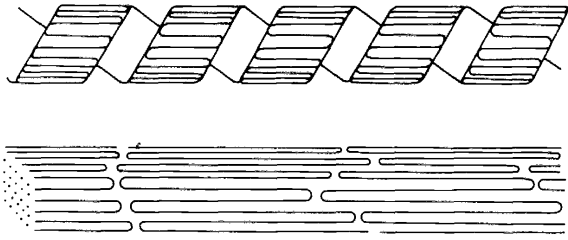


Figure 4. Proposed folded chain structure of elementary fibrils according to Manley¹⁶ and Marx-Figini and Schulz¹⁷.

theme for the cellulose chemist and a number of models were proposed to indicate the lateral order and detailed arrangement of the crystalline and amorphous regions. The micellar theory in turn was challenged with the idea of folded chain structure of cellulose molecules in quasicrystalline microfibrils, shown in *Figure 4*^{1, 16, 17}. Although the idea of the folded chain in its different forms was not generally accepted, the suggestion that the apparent presence of the intermittent amorphous and crystalline regions might be due to the misinterpretation of the x-ray diffraction, caused by crystal imperfection and surface scattering, has gained much ground irrespective of folded or extended chain configuration (see *Figure 5*)¹⁸.

In the meantime, development of the electron microscope brought a new insight into the structure of the microfibrils which were reported to vary

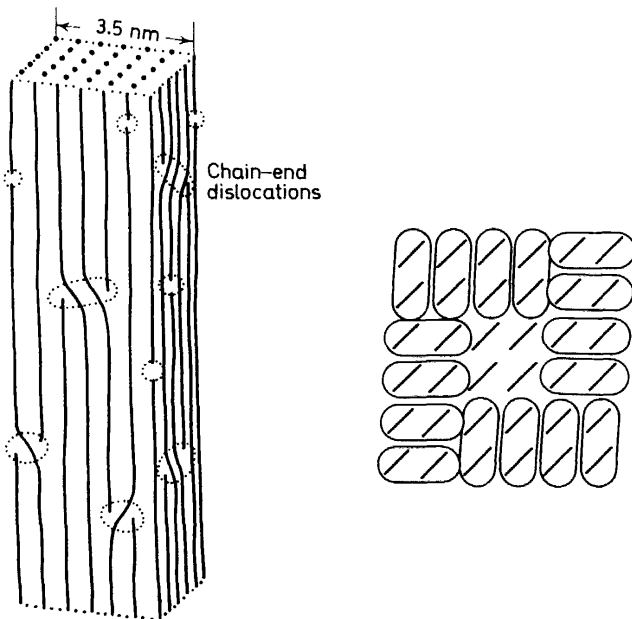


Figure 5. A recent concept of elementary fibrils proposed by Mühlethaler¹⁸.

from 30 to 8 nm in width. However, as the resolution of the electron microscope and operation methods improved, this value gradually was reduced to 3.5 nm and even less, until the very existence of uniform microfibrils were questioned as an artifact of electron microscopy.

As more and more information became available about the chemical structure of cellulose and its arrangement within the microfibrils as well as the orientation of the microfibrils within the intricate structure of the plant cell walls, it became a challenge to find out not only how these molecules are formed as a chemical entity, but also how they are packed in the fibrils and oriented to produce the unique architecture of the plant cell walls. The theories suggested to answer these questions fall into two general categories which have been hotly debated. Proponents of the deposition theories assume that precursors of cellulose in a 'prefibrous' or 'precrystalline' form are produced by the cell and transported to the proper location where they are crystallized and oriented by physical forces. Proponents of the apposition theory advocate that microfibrils are produced on the location as oriented microfibrils by end group synthesis.

Since extended chain structures are less likely to result from physical crystallizations of the polymers, the evidence for folded chain structure favours the deposition theory rather than the in-place end synthesis. On the other hand, it is harder to reconcile the end group synthesis with the proposed antiparallel crystalline structure of the cellulose molecule which is readily accounted for by the folded chain conformation.

When it was shown conclusively that the polysaccharides are biosynthesized from nucleotide precursors¹⁹, another controversy was added to the list. The new issue was whether cellulose is produced from UDP-D-glucose as shown in experiments with *Acetobacter xylinum* and *Lupinus albus* or from GDP-D-glucose as shown in experiments with mung bean (*Phaseolus aureus*) and maturing cottonballs.

The proposed theories and multidisciplinary discussions of this subject provide one of the most fascinating and controversial chapters of molecular science. The controversy in these considerations centres not only on the interpretation of the many physical and biological data, but also on the extent to which molecular and structural information could be used for understanding the biological processes and *vice versa*. While many of these questions and controversial theories are extant, the scientific lesson which they have already taught seems to be unequivocal. Looking in retrospect, there is little doubt that many of these controversies have originated from over simplification and consideration of a very complex natural system from a limited experimental point of view.

A broad consideration of this system which involves the entire kingdom of aquatic and land plants shows that the evolution and biogenesis of the polysaccharides are geared to the architecture and functions of the cell wall rather than merely to the formation of these materials as chemical entities. The formation of the cell wall in turn involves a programmed sequence of events including division, growth and differentiation which are executed through the agency of the cell organelles. Therefore, a better understanding of cellulosic materials could be derived not only through the investigation of the physical properties but also through the consideration of the archi-

CELLULOSE CHEMISTRY

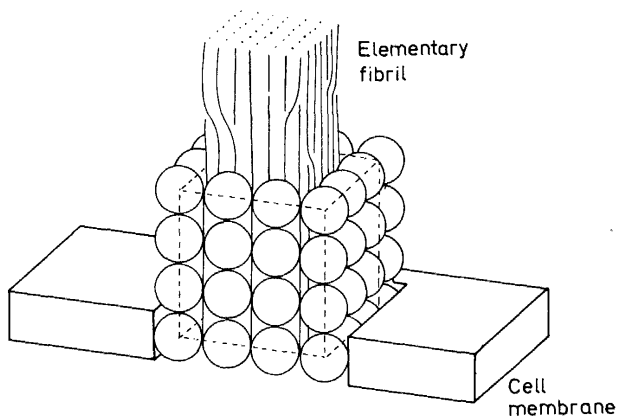


Figure 6. A model for biogenesis of cellulosic fibrils proposed by Mühlethaler¹⁸.

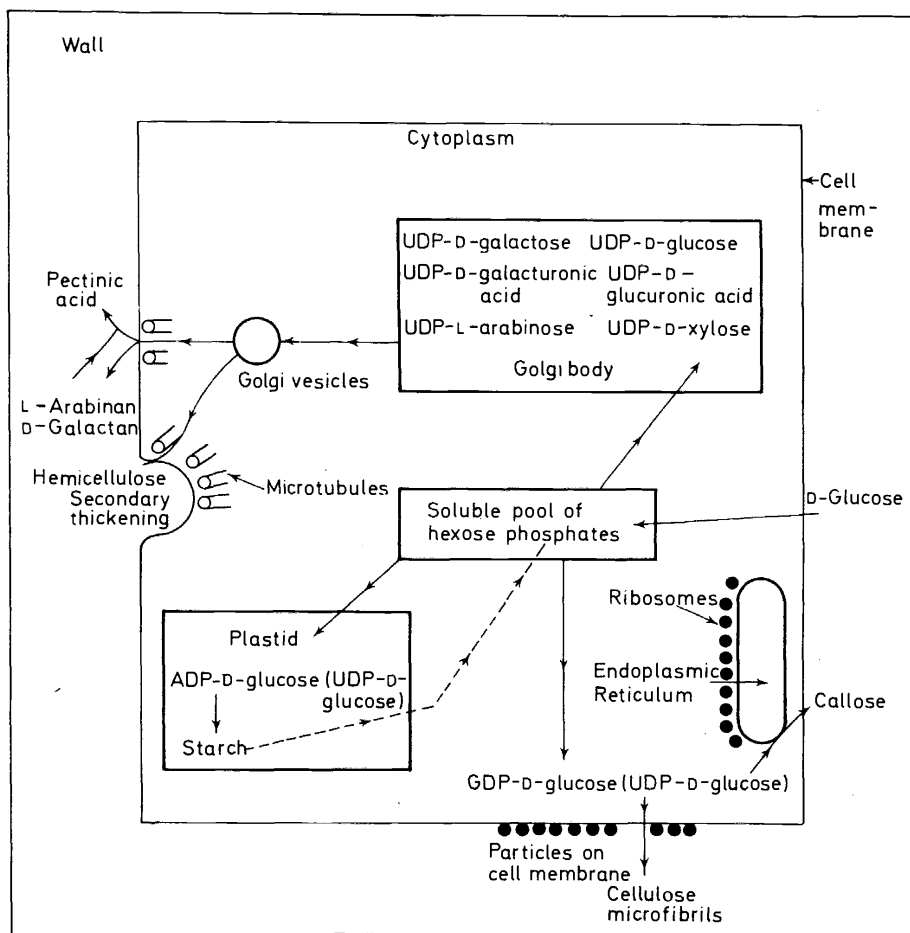


Figure 7. Diagrammatic presentation of the synthesis and transportation of various polysaccharides by Northcote²⁰

texture and function of the cell wall, as well as the role of the cell organelles in producing these materials. This approach has already shown that pectin and hemicelluloses which form the bulk of the primary wall are produced by Golgi bodies^{1, 20} within the cell and are directed and transported towards the cell wall as Golgi vacuoles. The cellulosic microfibrils that form the bulk of the secondary wall, however, are formed on the surface of the cell, by enzyme particles attached to the cell membrane or plasmalemma, as shown in *Figure 6*¹⁸. Other cell organelles, notably endoplasmic reticulum, plastids and microtubules, participate in the transportation, storage and location of the polysaccharides and their precursors as shown diagrammatically in *Figure 7*²⁰.

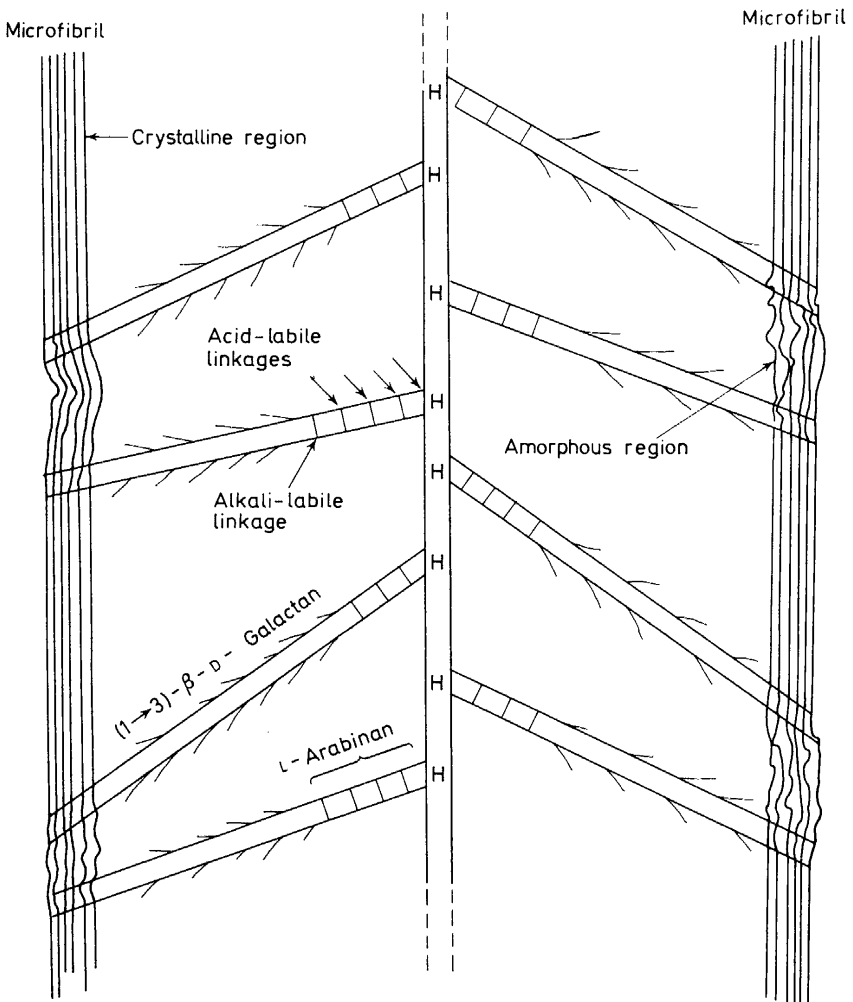


Figure 8. Hypothetical presentation of the glycoprotein network in plant cell walls, proposed by Lamport²¹.

One of the ramifications derived from the role of the Golgi bodies in production, packaging and transportation of polysaccharides and glycoproteins and the isolation of 4-hydroxy-L-proline-rich protein and glycoprotein from plant cell walls is that the matrix polysaccharides, contrary to the previous theory, are attached to a protein back bone as shown in *Figure 8*. The resulting glycoprotein system plays a significant role in the extension of the primary cell wall²¹.

THERMAL REACTIONS OF CELLULOSIC MATERIALS

Looking ahead, it seems clear that more emphasis will be placed on the understanding and investigation of cell wall polysaccharides as biological materials and significant environmental substrates. Unravelling the complex chemical reactions involved in the thermal transformation of cellulosic materials to flammable volatile products which lead to initiation and propagation of fire, may be cited as a case in point. Understanding the complex concurrent and consecutive thermal reactions is also receiving some attention for developing intelligent methods for disposal of the increasing amount of cellulosic wastes and their efficient conversion to more useful products. This type of basic investigation has been neglected before because of the complexity of the problem and the preference of scientists for neat isolated reactions carried out in suitable solvents at moderate temperatures. However, it has been recently shown that by combining the methods of thermal analysis with parallel chemical investigation and selection of closely related model compounds considerable information could be gained about the thermal cleavage of the glycosidic bonds and degradation of the sugar unit²²⁻²⁴. By controlling these reactions we may be able to cope with hazardous cellulosic fires and develop practical methods for management of cellulosic wastes.

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F. SHAFIZADEH

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